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# Local and global effects of quantum impurities on the quasiparticle tunneling spectra of p-type and n-type cuprate superconductors

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## ABSTRACT

We report scanning tunneling spectroscopic studies of the effects of quantum impurities on cuprate superconductors. The samples include p-type  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single crystals with spinless impurities of  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  ((Zn,Mg)-YBCO) and n-type infinite-layer system  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  with 1% magnetic  $\text{Ni}^{2+}$ - or 1% non-magnetic  $\text{Zn}^{2+}$ -impurities that substitute the  $\text{Cu}^{2+}$  in the  $\text{CuO}_2$  plane. The local effects of spinless impurities on the quasiparticles spectra of (Zn,Mg)-YBCO are analogous to those of Zn-substituted  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ , and the global effect is manifested by the suppression of the pairing potential  $\Delta_d$  and of the spin excitation energy. In contrast, spectroscopic studies of  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  reveal momentum-independent spectra and superconducting gap  $\Delta$ , with  $(2\Delta/k_B T_c) \sim 7$  for  $T_c = 43$  K and no pseudogap above  $T_c$ . The global response of  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  to quantum impurities is similar to that of *s*-wave superconductors, being insensitive to small concentrations of spinless impurities (Zn) while showing rapid degradation in  $T_c$  with increasing magnetic impurities (Ni). Moreover, the spectra of the Ni-substituted  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  reveal strong electron-hole asymmetry and long-range impurity effects, in contrast to the localized impurity effects in the p-type cuprates, and the introduction of Zn yield no reduction in either  $\Delta$  or  $T_c$ . The physical implications of these findings are discussed.

**Keywords:** scanning tunneling spectroscopy (STS), cuprate superconductors, pairing symmetry, quantum impurities, Kondo effect.

## 1. INTRODUCTION

Magnetic quantum impurities are known to suppress conventional superconductivity, and the detailed effects have been a topic of great research interest over the years<sup>1-6</sup>. In contrast, non-magnetic impurities in the dilute limit appear to inflict negligible effects on conventional superconductivity, as explained by the Anderson theory for dirty superconductors<sup>7</sup>. However, recent findings of strong effects of spinless quantum impurities on the hole-doped (p-type) cuprate superconductors<sup>8-22</sup> have rekindled active investigation on the effects of quantum impurities on superconductivity. In particular, theoretical studies have suggested that the effects of quantum impurities depend on the pairing symmetry and the existence of magnetic correlation in cuprate superconductors<sup>23-31</sup>. For instance, Fermionic nodal quasiparticles in the cuprates with either  $d_{x^2-y^2}$  or  $(d_{x^2-y^2}+s)$  pairing symmetry can interact strongly with the quantum impurities in the  $\text{CuO}_2$  planes and incur significant suppression of superconductivity regardless of the spin configuration of the impurity<sup>23-27</sup>. This phenomenon is in contrast to the insensitivity to spinless impurities in conventional *s*-wave superconductors<sup>7</sup>. Moreover, the spatial evolution of the quasiparticle spectra near quantum impurities would differ significantly if a small component of complex order parameter existed in the cuprate. For instance, should the pairing symmetry contain a complex component such as  $(d_{x^2-y^2}+id_{xy})$  that broke the time-reversal ( $\mathcal{T}$ ) symmetry, the quasiparticle spectrum at a spinless impurity site would reveal two resonant scattering peaks at energies of equal magnitude but opposite signs in the electron-like and hole-like quasiparticle branches<sup>24</sup>. In contrast, for either  $d_{x^2-y^2}$  or  $(d_{x^2-y^2}+s)$  pairing symmetry<sup>20-22,32-35</sup>, only one resonant scattering peak at the impurity site is expected<sup>23,25-27</sup>. In addition, the existence of nearest-neighbor antiferromagnetic  $\text{Cu}^{2+}$ - $\text{Cu}^{2+}$  correlation in the superconducting state of the cuprates can result in an unusual Kondo-like

behavior near a spinless impurity<sup>28–30</sup> due to an induced spin-1/2 ( $S = 1/2$ ) moment when one of the  $\text{Cu}^{2+}$  ions is substituted with a spinless ion such as  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Li}^+$ .<sup>8–22</sup> Indeed, the Kondo-like behavior associated with isolated spinless impurities in p-type cuprates has been confirmed from the nuclear magnetic resonance (NMR)<sup>8,9,17</sup> and the inelastic neutron scattering (INS) experiments<sup>14,15</sup>, and the spinless impurities are found to have more significant effects on broadening the NMR linewidth, damping the collective magnetic excitations and reducing the superfluid density than magnetic impurities such as  $\text{Ni}^{2+}$  with  $S = 1$ .<sup>8–22</sup> On the other hand, both types of impurities exhibit similar effects on suppressing superconducting transition temperature ( $T_c$ ), increasing the microwave surface resistance in the superconducting state and increasing the normal state resistivity.<sup>8–22</sup> The overall stronger suppression of superconductivity due to spinless impurities in *d*-wave cuprates has been attributed to the slower spatial relaxation of spin polarization near the spinless impurities than that near the  $S = 1$  impurities, the latter being partially screened by the surrounding antiferromagnetically coupled  $\text{Cu}^{2+}$  spins<sup>30,31</sup>. The detailed spatial evolution of the quasiparticle tunneling spectra near these quantum impurities in the cuprates can further provide useful insights into the pairing state of the cuprates, and has recently been investigated in impurity-substituted  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  systems using the low-temperature scanning tunneling microscopy (STM) techniques<sup>18–22</sup>. While in principle both the potential scattering and the Kondo effect contribute to the quasiparticle spectra near spinless impurities, which of the two scenarios may be dominating cannot be conclusively determined from existing data, because direct probing of the quasiparticle spectra near the quantum impurities using scanning tunneling spectroscopy (STS) involves not only the density of states in the  $\text{CuO}_2$  planes of the cuprates but also the tunneling matrix. The latter depends on the atomic nature of the surface layer and the exact path of the tunneling electrons, which is generally difficult to determine.

It is interesting to note that most research activities to date have been focused on the effects of quantum impurities in p-type cuprate superconductors<sup>8–31</sup>. Few reports associated with similar investigation on the n-type cuprates have been available until recently.<sup>36,37</sup> Given that the cuprate superconductors do not exhibit particle-hole symmetry and cannot be described by a simple one-band Hubbard model, it is essential to compare the effects of quantum impurities on the n-type cuprates with those on the p-type in order to achieve better understanding of the underlying pairing mechanism. For instance, the inapplicability of the one-band Hubbard model can be realized from the consideration of spin fluctuations in cuprate superconductors. In the p-type cuprates, holes are known to reside in the oxygen *p*-orbital of the  $\text{CuO}_2$  planes, which induces ferromagnetic coupling for the hole-linked  $\text{Cu}^{2+}$  spins thereby causing strong spin fluctuations in the antiferromagnetic host.<sup>38,39</sup> In contrast, excess electrons in the n-type cuprates reside in the copper *d*-orbital of the  $\text{CuO}_2$  planes, yielding spinless  $\text{Cu}^+$ -ions that dilute the background antiferromagnetism rather than causing severe spin fluctuations.<sup>40</sup> This example suggests the necessity of investigating both the p-type and n-type cuprates in order to identify universal features that are truly responsible for the occurrence of high-temperature superconductivity.

In this work, we report our recent scanning tunneling spectroscopic (STS) studies of optimally doped p-type and n-type cuprates with various quantum impurities, and compare our findings with other related experimental results. These investigations reveal that the response of cuprates to quantum impurities is indeed sensitive to the pairing symmetry and the type of the dopant, and that the only common features among all cuprates appear to be strong electronic correlation and background antiferromagnetism in the superconducting state.

## 2. QUANTUM IMPURITIES IN P-TYPE CUPRATE SUPERCONDUCTORS

### 2.1 General consideration of the effects of quantum impurities on *d*-wave superconductors

Experimental evidence to date has established that the p-type cuprates exhibit either pure  $d_{x^2-y^2}$  pairing symmetry in samples with tetragonal crystalline symmetry or  $(d_{x^2-y^2}+s)$  pairing symmetry in those with orthorhombic crystalline symmetry in the superconducting state.<sup>20–22,32–35</sup> The consequence of such pairing symmetries is that these cuprates are gapless along the  $(\pm\pi, \pm\pi)$  directions, hence substantial low-energy excitations in the form of nodal quasiparticles even at low temperatures. On the other hand, NMR experiments have clearly demonstrated that non-magnetic impurities that substituted the Cu-ions in the  $\text{CuO}_2$  planes can induce local  $S = 1/2$  moments on the neighboring Cu ions.<sup>9,17</sup> Moreover, magnetic impurities such as  $\text{Ni}^{2+}$  with  $S = 1$  naturally exhibit excess magnetic moments<sup>26</sup> despite the antiferromagnetic background with  $S = 1/2$  moments. These effective excess magnetic moments in the cuprate are expected to interact with the elementary excitations of the host, with particularly strong interaction with the existing nodal quasiparticles. Due to the complexity of many-body interactions in the strongly correlated electronic system, theoretical consideration for the

effect of quantum impurities has been limited to perturbative and one-band approximation, without self-consistently solving for the spatially varying pairing potential due to the presence of impurities.<sup>23–30</sup> Moreover, the interaction among impurities has been neglected. Thus, the Hamiltonian  $\mathcal{H}$  is approximated by  $\mathcal{H} = \mathcal{H}_{\text{BCS}} + \mathcal{H}_{\text{imp}}$ , where  $\mathcal{H}_{\text{BCS}}$  is the  $d$ -wave BCS Hamiltonian that contains the normal (diagonal) one-band single-particle eigen-energy and anomalous (off-diagonal)  $d_{x^2-y^2}$ -wave pairing potential  $\Delta_k (= \Delta_d \cos 2\theta_k$ ,  $\theta_k$  being the angle relative to the anti-node of the order parameter in the momentum space) of the unperturbed host, and  $\mathcal{H}_{\text{imp}} = \mathcal{H}_{\text{pot}} + \mathcal{H}_{\text{mag}}$  denotes the impurity perturbation due to both the localized potential scattering term  $\mathcal{H}_{\text{pot}} (= U \sum_{\sigma} c_{0\sigma}^{\dagger} c_{0\sigma})$ ;  $U$ : the on-site Coulomb scattering potential) and the Kondo-like magnetic exchange interaction term  $\mathcal{H}_{\text{mag}} (= \sum_{\mathbf{R}} J_{\mathbf{R}} \mathbf{S} \cdot \boldsymbol{\sigma}_{\mathbf{R}})$  between the spins of the conduction carriers on the  $\mathbf{R}$  sites ( $\boldsymbol{\sigma}_{\mathbf{R}}$ ) and those of the localized magnetic moments ( $\mathbf{S}$ ).

Assuming the aforementioned model Hamiltonian, one can obtain the quasiparticle spectra due to impurities by using the Green's function derived from  $\mathcal{H}$ . If one further neglects the contributions from the tunneling matrix, one obtain in the pure potential scattering limit a resonant energy at  $\Omega$  on the impurity site that satisfies the following relation<sup>23,24</sup>:

$$|\Omega/\Delta_d| \approx [(\pi/2) \cot \delta_0 / \ln(8/\pi \cot \delta_0)], \quad (1)$$

where  $\delta_0$  is the impurity-induced phase shift in the quasiparticle wavefunction. Generally  $\delta_0 \rightarrow (\pi/2)$  in the strong potential scattering (unitary) limit. On the other hand, in the case of magnetic impurities with both contributions from  $\mathcal{H}_{\text{pot}}$  and  $\mathcal{H}_{\text{mag}}$ , one expects two spin-polarized impurity states at energies  $\Omega_{1,2}$ , which are given by<sup>26</sup>:

$$|\Omega_{1,2}/\Delta_d| = 1/[2\mathcal{D}_F(U \pm W) \ln|8\mathcal{D}_F(U \pm W)|], \quad (2)$$

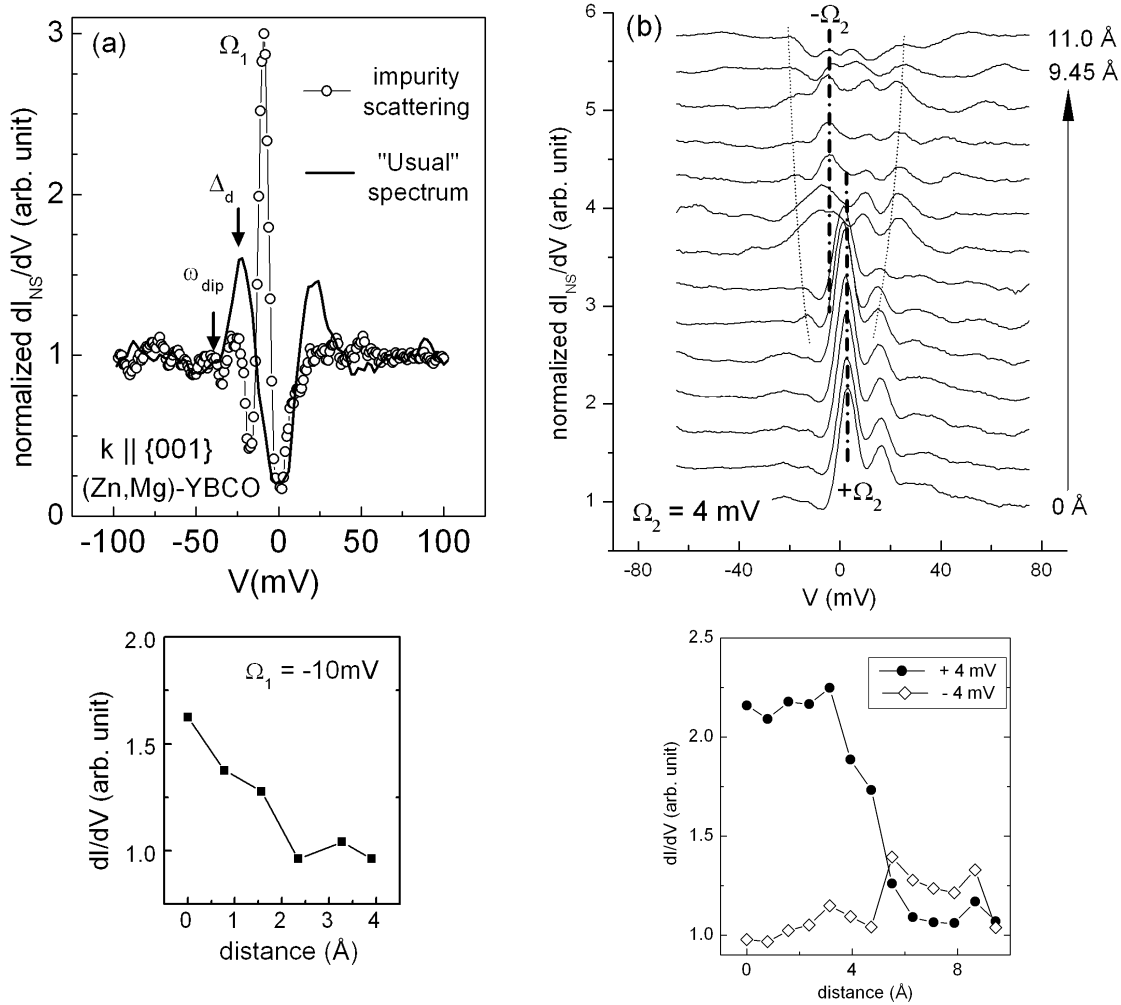
where  $\mathcal{D}_F$  is the density of states at the Fermi level and  $W \equiv JS \cdot \boldsymbol{\sigma}$  implies that magnetic impurities are isolated and equivalent at all sites. We remark that the assumption of non-interacting impurities is only valid in the limit of dilute impurities and strong screening due to conducting carriers.

## 2.2 STS studies of (Zn,Mg)-YBCO

We have performed STS studies on an optimally doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  (YBCO) single crystal with 0.26% Zn and 0.4% Mg substituted into the Cu sites in the  $\text{CuO}_2$  planes, hereafter denoted as (Zn,Mg)-YBCO. The superconducting transition temperature of the sample is  $T_c = 82.0$  K, which is substantially lower than that of the pure optimally doped YBCO with  $T_c = 93.0$  K. Additional STS studies on pure YBCO single crystals with different hole doping levels have also been performed for comparison with the impurity-substituted sample.<sup>20–22</sup> The quasiparticle tunneling spectra were taken with a low-temperature STM, and measurements on the (Zn,Mg)-YBCO have been concentrated on c-axis quasiparticle tunneling, while STS studies on other pure YBCO samples have been made along different crystalline axes, as reported elsewhere.<sup>20–22,34,35</sup> The measurements were taken at 4.2 K with a tunneling tip made of Pt(85%)-Ir(15%). The voltage resolution at 4.2 K was  $\sim 1$  meV, and the sample surface was prepared using a chemical etching process detailed before.<sup>20–22,34,35</sup> This process has been shown to yield reproducible and high-quality surface, as verified by both XPS and our extensive STS studies.<sup>20–22,34,35</sup>

The spectroscopic information obtained from the studies of (Zn,Mg)-YBCO is illustrated in Figure 1 and summarized as follows. For STM tip significantly far away from any impurities, the tunneling spectra were similar to the typical c-axis quasiparticle tunneling spectra in pure YBCO, as shown in the upper panel of Figure 1(a). However, we note that the global superconducting energy gap  $\Delta_d$  was suppressed to  $(25 \pm 2)$  meV from the value  $\Delta_d = (29 \pm 1)$  meV in pure YBCO.<sup>20–22</sup> Moreover, the energy  $\omega_{\text{dip}}$  associated with the "dip-hump" satellite features had also shifted substantially relative to that in pure YBCO. We note that the dip-hump feature has been attributed to effects of quasiparticle damping by the background many-body excitations such as spin fluctuations<sup>42,43</sup> or phonons<sup>44</sup>, and the resonant energy of the many-body excitation may be empirically given by  $|\Omega_{\text{res}}| = |\omega_{\text{dip}} - \Delta_d|$ . We find that the magnitude of  $\Omega_{\text{res}}$  in the (Zn,Mg)-YBCO sample decreased significantly to  $(7 \pm 1)$  meV from that in the pure YBCO where  $|\Omega_{\text{res}}| = (17 \pm 1)$  meV. This drastic decrease in  $\Omega_{\text{res}}$  with the very small impurity concentration in our (Zn,Mg)-YBCO has clearly ruled out phonons as the relevant many-body excitations to the satellite features. We can therefore associate the  $\omega_{\text{dip}}$  satellite feature with the presence of spin fluctuations in YBCO, and can also conclude that the presence of spinless impurities suppresses the  $\text{Cu}^{2+}$  spin fluctuations in the optimally doped  $d$ -wave cuprates.<sup>20–22</sup>

On the other hand, detailed studies on the surface of (Zn,Mg)-YBCO also revealed apparent impurity scattering spectra that could be associated with two types of impurities, with maximum scattering intensity occurring at either  $\Omega_1 \sim -10$  meV or  $\Omega_2 \sim 4$  meV.<sup>20–22</sup> By identifying the location of a maximum scattering intensity to the position of either a Zn or Mg impurity, we found that the intensity of the resonant scattering peak decreased rapidly within approximately one Fermi wavelength along the Cu-O bonding direction, as shown in the lower panels of Figures 1(a) and 1(b), while the coherence peaks associated with the superconducting gap were significantly suppressed, and the degree of suppression was asymmetric between the electron-like and hole-like branches. Moreover, with the STM tip moving away from the impurity site, the resonant scattering peak appeared to alternate between energies of the same magnitude and opposite signs, as exemplified in the upper panel of Figure 1(b). Such spatial variations are expected for both Kondo-like and charge-like impurities. However, some of these spatially varying spectra near impurities also revealed slow temporal variations over long times (about  $\sim 10^2$  s), which would have been more consistent with the Kondo effect. Finally, the impurity effects on the variations in the quasiparticle spectra appeared to have completely diminished at approximately two coherence lengths ( $\sim 3$  nm) away from the impurity, as shown in lower panel of Figure 1(b).



**Figure 1** Normalized c-axis differential conductance ( $dI/dV$ ) versus bias voltage ( $V$ ) quasiparticle tunneling spectra of the (Zn,Mg)-YBCO single crystal near impurity sites at 4.2 K. **(a) Upper panel:** A representative impurity scattering spectrum with a resonant peak at  $\Omega_1 \sim -10$  meV and a typical spectrum away from impurities. **Lower panel:** Spatial variation of the impurity-induced resonant peak intensity. **(b) Upper panel:** Representative spectra revealing spatial variations in the quasiparticle spectra along the Cu-O bonding direction from an impurity with a maximum scattering at  $\Omega_2 \sim +4$  meV. We note the alternating resonant peak energies between  $+4$  meV and  $-4$  meV and the particle-hole asymmetry in the degrees of suppression of the superconducting coherence peaks. **Lower panel:** Spatial variation of the impurity-induced resonant peak intensity, showing alternating peak intensities at energies  $+4$  meV and  $-4$  meV with distance from an impurity.

Independent of the dominating interaction of the impurity with quasiparticles, the resonant energy at  $\Omega_1 \sim -10$  meV can be associated with a weaker impurity than that at  $\Omega_2 \sim 4$  meV. This attribution can be verified by considering the following two extreme limits. If we assume pure potential scattering, we obtain a phase shift  $\delta_1 \sim 0.38\pi$  associated with  $\Omega_1$  and  $\delta_2 \sim 0.43\pi$  associated with  $\Omega_2$  by using Eq. (1), and the latter is clearly associated with a stronger scattering potential  $U$ . On the other hand, if we assume pure Kondo scattering effects, the resonant peak energy would be comparable to the corresponding Kondo temperature  $T_k$ ,<sup>29,30</sup> and the latter decreases with increasing exchange interaction. Hence, the impurity associated with the energy  $\Omega_2$  would correspond to stronger magnetic exchange interaction with the quasiparticles. Considering that  $\text{Mg}^{2+}$ -ions is likely to cause stronger structural distortion in the  $\text{CuO}_2$  planes than  $\text{Zn}^{2+}$ , we may tentatively assign  $\Omega_1$  to Zn-impurities and  $\Omega_2$  to Mg-impurities. This issue can be verified in the future by studying purely Zn-substituted YBCO and Mg-substituted YBCO.

**Table 1** Summary of the effects of spinless quantum impurities on the superconductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .<sup>18,20-22</sup>

Properties	$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Ref. 18)
Resonant scattering energy at the impurity site	$\text{Zn}^{2+}$ : $\Omega_1 = -10$ meV $\text{Mg}^{2+}$ : $\Omega_2 = +4$ meV	$\text{Zn}^{2+}$ : $\Omega = -1.5$ meV
Phase shift due to potential scattering	$\text{Zn}^{2+}$ : $\delta_1 \sim 0.38\pi$ $\text{Mg}^{2+}$ : $\delta_2 \sim 0.43\pi$	$\text{Zn}^{2+}$ : $\delta \sim 0.45\pi$
Spectral recovery length ( $\gamma^{-1}$ )	$\gamma^{-1} \sim 3.0$ nm (empirical) $\sim 2.5$ nm (theoretical)	$\gamma^{-1} \sim 1.5$ nm (empirical)
Global effect on the maximum $d$ -wave energy gap $\Delta_d$	$\Delta_d$ decreases from $(30 \pm 1)$ meV to $(25 \pm 2)$ meV.	unknown due to nanoscale spectral variations.
Global effect on the spin resonant energy $\Omega_{res}$	$\Omega_{res}$ decreases from $16 \sim 18$ meV to $8 \sim 10$ meV.	unknown due to nanoscale spectral variations.
Global effect on $T_c$	$T_c$ decreases from $\sim 93$ K to $\sim 82$ K.	$T_c$ decreases from $\sim 87$ K to $\sim 84$ K.
General remarks	weaker & longer-range impurity effects $\rightarrow$ stronger impurity correlation?	non-interacting impurities nearly in the unitary limit.
	both potential scattering and Kondo effect appear to be relevant.	more consistent with potential scattering.
	$\mathcal{T}$ -symmetry is preserved.	$\mathcal{T}$ -symmetry is preserved.

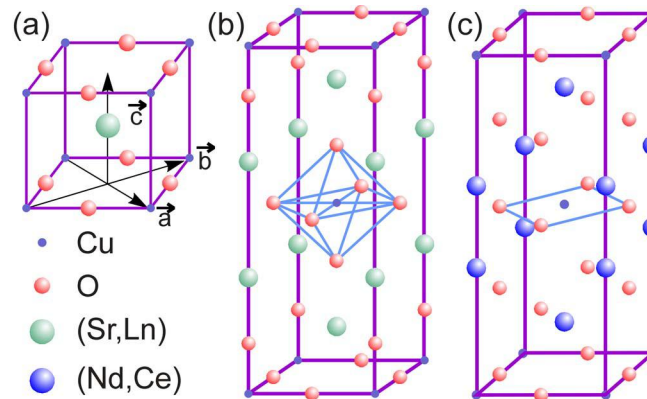
### 2.3 Comparing the Effect of Non-Magnetic Quantum Impurities in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

Next, we compare our findings derived from the (Zn,Mg)-YBCO sample with similar STS studies of a 0.6% Zn-substituted  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (BSCCO).<sup>18</sup> Generally speaking, the primary features such as the appearance of single resonant scattering peak and strong suppression of the superconducting coherence peaks at the impurity site, as well as the rapidly decreasing intensity of the resonant peak with the displacement from the impurity site, are comparable in both systems. These findings are also consistent with the preservation of time-reversal ( $\mathcal{T}$ ) symmetry in both systems, suggesting the absence of any discernible complex order parameter in the pairing symmetry. On the other hand, several differences are noteworthy. First, the strength of impurity scattering appears weaker and longer-ranged in YBCO.

Second, various phenomena that are more consistent with the Kondo effect, such as alternating resonant peak energies between  $+\Omega$  and  $-\Omega$  with the distance from a spinless impurity and temporal variations of the resonant peak, have only been observed in YBCO. Third, global suppression of the superconducting energy gap and of the collective magnetic excitation energy has only been revealed in YBCO. Such a difference may be attributed to the fact that pure YBCO generally exhibits long-range spectral homogeneity, whereas nanoscale spectral variations have been reported in nominally pure BSCCO samples, yielding difficulties in identifying the global effect of impurity substitutions. The similarities and differences between the effects of spinless impurities on YBCO and those on BSCCO are summarized below in Table 1.

### 3. QUANTUM IMPURITIES IN N-TYPE CUPRATE SUPERCONDUCTORS

As stated in the introduction, most studies of the impurity effects on the cuprate superconductors have focused on the p-type cuprates. We shall consider in the following the effects of quantum impurities on the simplest form of cuprates, known as the n-type infinite-layer system. However, it is necessary to first address several issues of general importance and relevance to all n-type cuprates, particularly in light of various competing orders in the cuprates<sup>38–40</sup> that are extremely sensitive to the fine tuning of structural variations and doping levels. In this context, it is informative to compare the structures of the representative p-type and n-type cuprates, as shown below in Figure 2. Generally speaking, the most significant structural difference between n-type and p-type cuprates is that all p-type cuprates have apical oxygen associated with the Cu atoms in the  $\text{CuO}_2$  planes, whereas no apical oxygen exists along the c-axis of all n-type cuprates<sup>41</sup>. A very important effect of the presence of apical oxygen is that it lifts the energy degeneracy between the  $d_{x^2-y^2}$ -orbital and the  $d_{3z^2-r^2}$ -orbital, with the former lower in energy for holes. This phenomenon can play an important role in the determination of the pairing symmetry in various cuprates, as discussed in the following.



**Figure 2** Crystalline structures of representative cuprates: (a) The n-type infinite-layer system  $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_2$ , with  $\text{Ln} = \text{La}, \text{Gd}$ , and  $\text{Sm}$ . (b) The one-layer p-type system  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . (c) The one-layer n-type system  $\text{R}_{2-x}\text{M}_x\text{CuO}_4$ , with  $\text{R} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$ ;  $\text{M} = \text{Ce}, \text{Th}$ .

#### 3.1 Pairing symmetry in n-type cuprates

The pairing symmetry in the one-layer n-type cuprates has been controversial, with different experiments suggesting either  $s$ -wave or  $d_{x^2-y^2}$ -wave pairing symmetry<sup>45,46</sup>. Noting that the undoped cuprates are Mott antiferromagnetic insulators with very large on-site Coulomb repulsion<sup>38–40</sup> and that a large charge reservoir exists between the  $\text{CuO}_2$  planes and the Cu atoms in each  $\text{CuO}_2$  plane of all p-type cuprates are connected to apical oxygen, it seems reasonable that the pairing symmetry favors  $d_{x^2-y^2}$ -wave over  $s$ -wave in most p-type cuprates so that the on-site Coulomb repulsion and orbital potential energy can be minimized while maintaining the quasi two dimensionality of the system. On the other hand, the absence of apical oxygen in the n-type cuprates results in degenerate  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  orbital so that the benefit of forming  $d_{x^2-y^2}$ -wave pairing is reduced, although the significantly large separation between consecutive  $\text{CuO}_2$  planes in the one-layer n-type cuprates could still favor a pairing symmetry that preserves the quasi-two dimensionality.

The exact pairing symmetry in a specific sample may therefore depend sensitively on the subtle balance of various competing energy scales. Indeed, it has been suggested recently that the pairing symmetry in the one-layer n-type cuprates can be either  $s$ -wave or  $d_{x^2-y^2}$ -wave, depending on the electron doping level.<sup>47</sup> This proposed doping dependence could in fact account for the controversies surrounding the pairing symmetry of the one-layer n-type cuprates.<sup>45,46</sup>

On the other hand, the infinite-layer n-type cuprate  $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_2$  ( $\text{Ln} = \text{La}, \text{Gd}, \text{Sm}$ ), known as the simplest form among all cuprate superconductors,<sup>48-50</sup> has several unique characteristics that differ from other cuprates and may in fact favor  $s$ -wave pairing. First, in contrast to all other cuprates with a large charge reservoir between the  $\text{CuO}_2$  planes, the infinite-layer system only contains a metallic monolayer of  $\text{La}(\text{Sr})$  between consecutive  $\text{CuO}_2$  planes. Second, the  $c$ -axis superconducting coherence length ( $\xi_c \sim 0.53$  nm) is longer than the  $c$ -axis lattice constant ( $c_0$ ),<sup>51</sup> in contrast to the typical condition of  $\xi_c \ll c_0$  in most other cuprates. Hence, the infinite-layer system is expected to reveal characteristics more like a three-dimensional superconductor. Third, it is found from the Knight shift experiments<sup>52</sup> that the carrier density of the optimally doped  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  at the Fermi level is significantly smaller than that in typical p-type cuprates, being  $\sim 25\%$  that of optimally doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ . These atypical characteristics of the infinite-layer system are suggestive of a stronger tendency toward more isotropic pairing symmetry as well as weak screening and strong electronic correlation, and are therefore worthy of careful investigation.

### 3.2 Evidence of strongly correlated $s$ -wave superconductivity in pure $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$

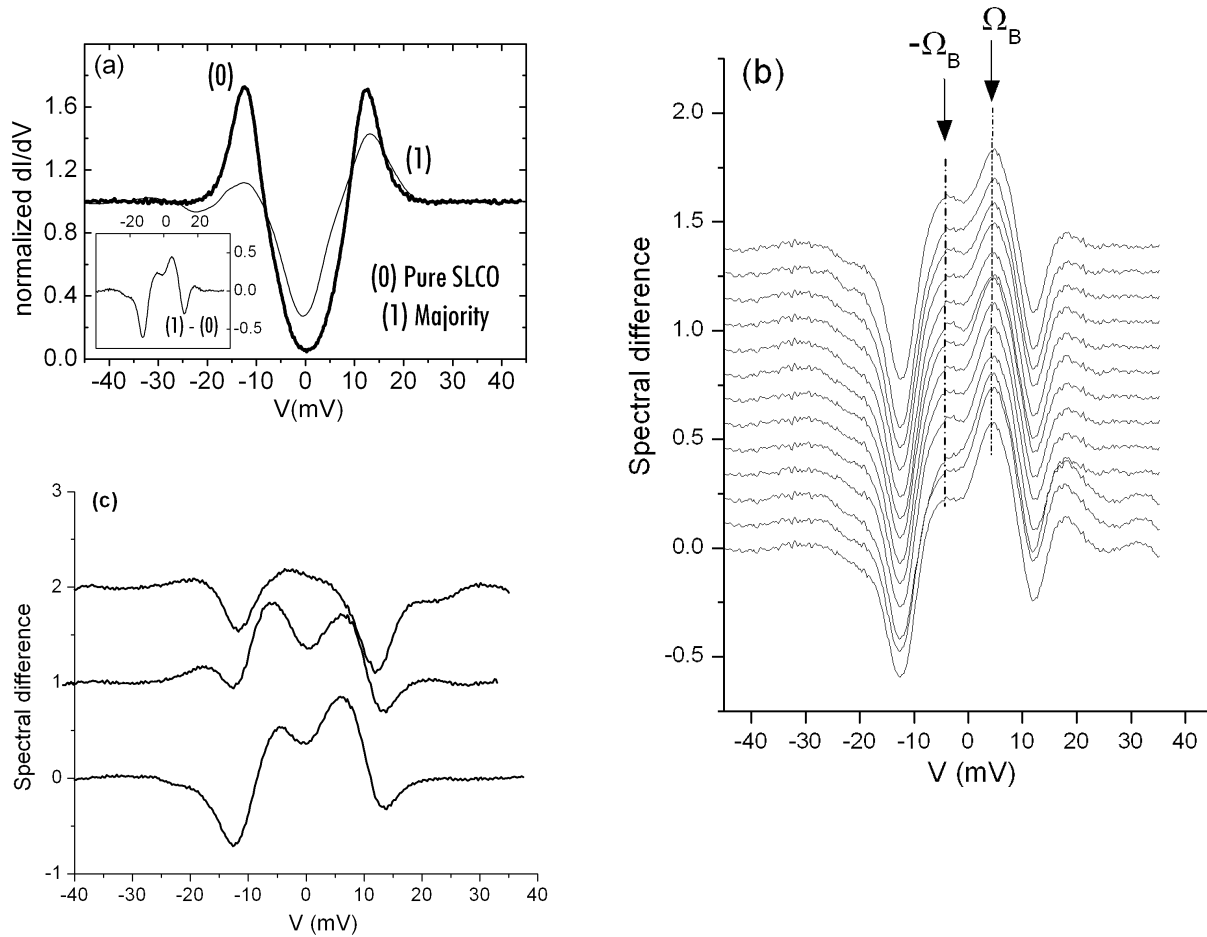
Despite the importance of understanding the infinite-layer cuprates, these materials are very difficult to synthesize, and the lack of single-phased compounds with high volume fraction of superconductivity<sup>48-50</sup> has hampered the research until a recent breakthrough.<sup>51</sup> Using high-pressure ( $\sim 4$  GPa) and high-temperature ( $\sim 2000$  °C) annealing conditions, Jung *et al.* have been able to routinely achieve single-phased  $\text{Sr}_{0.9}\text{Ln}_{0.1}\text{CuO}_2$  compounds with nearly  $\sim 100\%$  superconducting volume.<sup>51</sup> With the availability of these high-quality infinite-layer cuprates, it has finally become possible for us to perform scanning tunneling spectroscopic studies to investigate the quasiparticle tunneling spectra and the pairing symmetry. Our recent STS studies on the optimally doped  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  system have revealed a number of curious phenomena that defy various widely accepted scenarios in p-type cuprate superconductors.<sup>36</sup> First, the quasiparticle tunneling spectra and the superconducting energy gap  $\Delta$  appear to be momentum-independent, and the ratio of  $(2\Delta/k_B T_c) \sim 7$  for  $T_c = 43$  K is much larger than the BCS ratio ( $\sim 3.5$ ) for weak coupling  $s$ -wave superconductors. Moreover, no discernible satellite features exist in the quasiparticle spectra, in sharp contrast to those of all p-type cuprates, as exemplified by the thick curve in Figure 3(a) for a representative spectrum taken on the optimally doped  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ . In addition, the superconducting coherence peaks completely vanish above  $T_c$ , suggesting the absence of pseudogap<sup>38,39,53</sup>, which has also been independently verified by NMR experiments<sup>52</sup> on similar samples. Combined with recent confirmation of complete absence of pseudogap phenomena in various one-layer n-type cuprates with different doping levels<sup>54</sup> and the lack of universal pairing symmetries in all cuprates, it may be suggested that the pseudogap phenomena and  $d_{x^2-y^2}$ -wave pairing symmetry in most p-type cuprates are the consequence of competing orders rather than the sufficient conditions for cuprate superconductivity. In this context, it seems particularly interesting to investigate how the infinite-layer cuprates respond to various quantum impurities in the Cu sites.

### 3.3 Effects of quantum impurities on the infinite-layer system

As discussed in the previous sections, cuprates with  $d_{x^2-y^2}$ -wave pairing symmetry are strongly affected by both magnetic and non-magnetic quantum impurities in the  $\text{CuO}_2$  planes. On the other hand, superconductors with  $s$ -wave pairing symmetry are expected to be insensitive to a small concentration of non-magnetic impurities due to the fully gapped Fermi surface and therefore limited interaction with the low-energy excitations at low temperatures.<sup>7</sup> It is therefore natural to further substantiate the unusual finding of  $s$ -wave pairing symmetry in the infinite-layer system by investigating the effect of quantum impurities on its superconductivity. Indeed, our bulk magnetization studies<sup>37</sup> revealed that the substitution of spinless Zn-impurities into the Cu sites of  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  was found to yield no suppression in the bulk  $T_c$  up to 3% impurities, beyond which the compound became inhomogeneous and phase segregated. On the other hand, the substitution of magnetic Ni-impurities into the Cu sites of  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  yielded significant  $T_c$  suppression. With 1% Ni,  $T_c$  already decreased from 43 K to 32 K; 2% Ni dropped  $T_c$  to below 4 K, and 3% Ni completely suppressed the bulk superconductivity although the sample was still stoichiometrically homogeneous from x-ray diffraction. Hence,



the response of the  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  system to quantum impurities appeared to differ significantly from that of p-type cuprates<sup>8–22</sup> and was analogous to that of conventional s-wave superconductors<sup>4,6</sup>. In this context, we may apply the Abrikosov-Gor'kov theory<sup>1</sup> for magnetic impurities in conventional superconductors to estimate the exchange interaction energy  $J$  between the magnetic impurity and the conduction electrons. Using the relation  $(xJ^2/E_F) \sim \Delta$  where  $x$  denotes the critical concentration of magnetic impurities for complete suppression of superconductivity and  $E_F$  is the Fermi energy,<sup>1</sup> we obtain  $J \approx 0.28$  eV if we take the empirical values of  $x \approx 0.03$  and  $\Delta \approx 13$  meV, and also assume a reasonable value of  $E_F \approx 0.2$  eV for  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ . This exchange energy is comparable to but somewhat larger than the  $\text{Cu}^{2+}$ - $\text{Cu}^{2+}$  antiferromagnetic coupling constant.



**Figure 3** Quasiparticle tunneling spectra of the infinite-layer system at 4.2 K. **(a)** Comparison of the spectrum taken on a pure  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  (thick line) and that on a 1% Ni-substituted  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  (thin line). The inset illustrates the spectral difference of the two spectra in the main panel, which corresponds to the  $S = 1$  Ni-impurity contributions. **(b)** Long-range spatial extension of the impurity spectral contribution is shown over  $\sim 30$  nm. The spatial separation between two consecutive curves was 3 nm, and the spectra were shifted vertically in the graph for clarity. These spectra appeared to be quite homogeneous over long range within one grain, although slight spectral variations existed. Two asymmetric bound-state energies in the electron-like and hole-like branches were visible at  $|\Omega_B| \sim 5$  meV. **(c)** Other representative spectral contributions from Ni-impurities in different grains, showing some variations from grain to grain. The origin for such variations is unknown, and may be related to inhomogeneous Ni concentrations.

Our spectroscopic studies<sup>36</sup> of 1% Zn-substituted  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  and 1% Ni-substituted  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  further corroborated earlier findings from the bulk magnetization measurements<sup>37</sup>. That is, the tunneling spectra taken on 1% Zn-substituted  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  appeared to be spatially homogeneous, with no suppression in the superconducting gap value although the quasiparticle lifetime was reduced due to Zn-induced disorder in the sample. In contrast, detailed

spectroscopic studies on the 1% Ni-substituted  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  revealed quasiparticle spectra with large electron-hole asymmetry, as shown by a representative spectrum in Figure 3(a). The spectral difference between the 1% Ni-substituted  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  and the pure  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  is shown in the inset of Figure 3(a), which represents the impurity contribution to an effective bound state, known as the Shiba state in conventional superconductivity. We further notice that the impurity contribution appeared to extend over a relatively long range, as exemplified in Figure 3(b) where consecutive tunneling spectra taken at  $\sim 3$  nm apart on the same grain are shown. Studies over many grains consistently revealed that the Ni-impurities contributed to a bound state at energies  $\pm \Omega_B$  where the average value over all grains yielded  $|\Omega_B| = (5 \pm 2)$  meV. While slight variations can be observed in the impurity-induced bound state from one grain to another, overall the bound-state spectral contribution appeared to be quite consistent over a long range. This finding is in sharp contrast to the rapidly vanishing effects of magnetic impurities at approximately one Fermi wavelength away from an isolated Mn or Gd atom on Nb-superconductor. We attribute the difference to the weak screening effect of the infinite-layer system, and also to the strong overlap of the Ni-impurity wavefunctions. That is, the average Ni-Ni separation for 1% Ni-substitution in  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  is  $d_{\text{Ni}} \sim 1.8$  nm in the  $\text{CuO}_2$  planes and  $\sim 1.6$  nm along the  $c$ -axis, whereas the spatial extension ( $\xi$ ) of the impurity wavefunction can be estimated using the following formula<sup>1,2,5</sup>:

$$\xi = \xi_0 \Delta / (\Delta^2 - \Omega_B^2)^{1/2}, \quad (3)$$

with  $\xi_0$  being the BCS coherence length at  $T = 0$ . Using the anisotropic superconducting coherence lengths<sup>37,51,55</sup>  $\xi_{\text{ab}} \approx 4.8$  nm and  $\xi_c \approx 0.53$  nm, also using  $|\Omega_B| \approx 5$  meV and  $\Delta \approx 13$  meV, we estimate the in-plane spatial extension of the impurity wavefunction as  $\xi_{\perp} \approx 5.2$  nm  $\sim 3 d_{\text{Ni}}$  while the  $c$ -axis wavefunction extension is  $\xi_{\parallel} \approx 0.58$  nm  $\sim 0.4 d_{\text{Ni}}$ . This simple estimate suggests that there is substantial overlap of impurity wavefunctions. Thus, the effects of 1% Ni substitution in  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  should be considered as a Kondo alloy rather than a typical Kondo problem for isolated magnetic impurities.

Comparing the magnetic impurity effects on the  $n$ -type infinite-layer system with the STS studies of Ni-substitution in the  $p$ -type cuprate  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ,<sup>19</sup> we note that the latter revealed relatively short-range impurity effects and two bound state energies at  $\pm \Omega_1$  and  $\pm \Omega_2$ , where  $|\Omega_1| = (9.2 \pm 1.1)$  meV and  $|\Omega_2| = (18.6 \pm 0.7)$  meV. Furthermore, the potential scattering effects of Ni on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  appeared to be more significant than the Kondo effect,<sup>19</sup> whereas in the  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  system the potential scattering seemed less relevant, as manifested by the insignificant Zn-impurity effects on the superconductivity of  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ . The relatively insignificant potential scattering effect on the infinite-layer system may be understood in terms of the  $s$ -wave pairing that ensures a fully gapped Fermi surface at low temperatures and therefore insensitivity to the non-magnetic disorder<sup>7</sup>. In Table 2 we summarize the effects of Ni-substitutions on the  $n$ -type  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  system and compare them with those on the  $p$ -type cuprate  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .

**Table 2** Comparison of the effects of Ni-impurities on the  $n$ -type  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  and on the  $p$ -type  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .

Properties	$\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$	$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Ref. 19)
Pairing symmetry	$s$ -wave	$d_{x^2-y^2}$ -wave
Impurity bound-state energies	$ \Omega_B  = (5 \pm 2)$ meV	$ \Omega_1  = (9.2 \pm 1.1)$ meV $ \Omega_2  = (18.6 \pm 0.7)$ meV
Effective range of magnetic impurities	long range ( $\sim 10^2$ nm)	short range ( $< \sim 3$ nm)
Global effect of Ni on the transition temperature $T_c$	$T_c$ : 0% -- 43 K, 1% -- 32 K, 2% -- $\leq 4$ K, 3% -- 0 K.	$T_c$ : 0% -- 95 K, 0.2% -- 85 K 0.5% -- 83 K.
Cause for the suppression of superconductivity	broken particle-hole symmetry due to collective Kondo effect; $J = 0.2 \sim 0.3$ eV.	more significant potential scattering than the Kondo effect.

Finally, we remark on the apparent absence of induced magnetic moments due to Zn-substitution in  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ , as opposed to the situation in p-type cuprates.<sup>9,17</sup> By considering the available electronic configurations for the outer orbitals of the cations in the  $\text{CuO}_2$  plane, it seems feasible that a  $\text{Zn}^{2+}$  substitution in the n-type cuprates tends to localize of a spinless  $\text{Cu}^+$ -ion to its neighboring site. Thus, no excess magnetic moments are formed due to Zn-substitution in the n-type cuprates, and the corresponding perturbation to both the spin and orbital degrees of freedom is minimized.

#### 4. SUMMARY

We have investigated the effects of magnetic and non-magnetic quantum impurities on the quasiparticle tunneling spectra of both p-type and n-type cuprate superconductors. In the case of optimally doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ , we find that the introduction of spinless impurities such as Zn or Mg results in global suppression of the superconducting energy gap and the spin fluctuations. Furthermore, the local quasiparticle spectra near impurities reveal interesting spatial variations that are similar to the findings from the Zn-substituted  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.8}$ , although the spinless impurities appear to extend over longer spatial range and also weaker in the impurity scattering strength in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  system. The occasional observation of long-time temporal variations in the latter suggests that the Kondo effect induced by the spinless impurities may be more significant than the potential scattering effect in  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ . The overall strong response of p-type cuprates to both the magnetic and non-magnetic impurities can be attributed to the  $d_{x^2-y^2}$ -wave pairing symmetry and the existence of background antiferromagnetic correlation. On the other hand, our investigation of the quantum impurity effects on the simplest cuprate  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ , known as the n-type infinite-layer system, reveals results that are in general consistent with s-wave superconductors. That is, both the global  $T_c$  and the local quasiparticle spectra of the  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  system appear insensitive to spinless impurities such as  $\text{Zn}^{2+}$  while showing significant suppression of superconductivity with  $\text{Ni}^{2+}$  substitution. However, the magnetic impurities in  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  manifest substantial overlap in their wavefunctions, yielding long-range electron-hole asymmetry in the quasiparticle spectra. Such observation of impurity effects is consistent with our other findings of momentum-independent quasiparticle spectra and strong electronic correlation in the pure  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  system. These detailed comparisons between the p-type and n-type cuprates led us to conclude that various widely accepted characteristics such as the  $d_{x^2-y^2}$ -wave pairing symmetry, spin fluctuations and pseudogap phenomena are not truly universal among all cuprates. Rather, they are likely the consequences of competing orders. The only ubiquitous features among all cuprates appear to be the strong electronic correlation and the background antiferromagnetic coupling.

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